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CATION-EXCHANGERS FROM CROSS-LINKED POLYHYDROXY MATERIALS

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This is a continuation-in-part of our application Serial No. 34,374, filed June 7, 1960, and now abandoned.

The invention generally pertains to substitution products of hydrophilic high molecular weight copolymerizates of aliphatic hydroxyl group-containing substances with bifunctional organic substances. More particularly, this invention relates to substitution products of hydrophilic high molecular weight copolymerizates of aliphatic hydroxyl group-containing substances with bifunctional organic substances, obtained by reacting the hydroxyl groups of the copolymerizates with a monofunctional substance to form novel products possessing valuable properties for different uses and especially useful as cation-exchangers for separating purposes.

In the specification and the claims the term "copolymerizate" is used to define a product obtained by the chemical combination of a number of similar units to form a single molecule, wherein polymerization phenomena as well as condensation reactions have been involved.

THE INVENTION BROADLY

The novel products according to the present invention are copolymerizates of:

(*a*) A member selected from the group consisting of dextran, sucrose, starch, sorbitol, dextrin, polyvinyl alcohol, and hydroxyethyl cellulose;

(*b*) A bifunctional organic substance selected from the group consisting of epichlorohydrin, bis-epoxypropyl-ether and ethylene glycol-bis-epoxy propyl ether which is capable of linking together the aforesaid members by the formation of ether linkages;

(*c*) Said copolymerizate orginally containing from 10 to 35 percent of hydroxyl groups, based on the weight of the dry substance, and having from 6 to 50 percent of their hydroxyl groups originally present in the formation substituted by a member selected from the group consisting of radicals of the type R_1Y, wherein

(*d*) R_1 is an alkylene containing from one to two, inclusive, carbon atoms, and

(*e*) Y is selected from the group consisting of carboxyl and sulfo; and said novel compound,

(*f*) Being insoluble in water but capable of swelling therein;

(*g*) Having a waterregain within the range of 1–50 grams per gram of the dry compound, and

(*h*) Having an ion-exchange capacity within the range of from 2 to 6 milliequivalents per gram of the dry compound.

From physical viewpoint, the novel substituted copolymerizates consist of a three-dimensional macroscopic network of residues of the aliphatic hydroxyl group-containing substances, bonded together by ether bridges of the formula —R—O—X—O—R—, wherein R represents the residue of the aliphatic hydroxyl group-containing substance and X is a residue of the bifunctional substance, the said copolymerizates having connected thereto by oxygen bridges groups of the general formula $—R_1Y$, wherein R_1 and Y each have the above significance. In addition to the substituted copolymerizates as substances, the invention also includes cation-exchangers consisting of these substances.

The novel substituted copolymerizates according to the invention are obtained by reacting the unsubstituted copolymerizate of the type referred to with a monofunctional substance of the formula $X_1—R_1—Y$, wherein X_1 is selected from the group consisting of chloro and bromo and R_1 and Y have the significances set forth above. However, it is also possible to prepare the novel compounds by first reacting one of the members listed under (*a*) above with the monofunctional substance of the formula $X_1—R_1—Y$ to introduce the ion-exchanging groups and then carrying out the copolymerization process.

THE HYDROPHILIC HIGH MOLECULAR WEIGHT COPOLYMERIZATE

The hydrophilic high molecular weight copolymerizate used as a starting material for the preparation of the substituted product according to the invention should have a high content of hydroxyl groups. Preferably this content should be in the range of about 10 to 35 percent.

The particle size of the starting material should preferably be in the range of 0.01 to 2 mm.

The water regain of the starting material should be in the range of from 1 to 50 g./g. of the dry copolymerizate. The term "water regain" is intended to mean the amount of water in grams which can be absorbed by 1 g. of the dry condensation product with swelling. The starting material should not contain any charge-producing groups.

The copolymerizates to be used as a starting material for the production of the novel products are obtained by reacting the polyhydroxyl compounds set forth above with the bifunctional organic compounds.

The copolymerization of these organic hydroxyl group-containing substances with the bifunctional substances readily takes place by reacting the components in aqueous solution in the presence of an alkaline reacting substance as a catalyst.

For example, a gel product excellently suitable as a starting material to produce the novel ion-exchangers according to the invention may be obtained by reacting dextram having an average molecular weight within the range of from 20,000 to 100,000 with epichlorohydrin which results in a copolymerization consisting of a three-dimensional macroscopic network, built up of chains of mainly alpha-1,6-glycosidically bonded glucose residues bound together by ether bridges of the type

$$—O—CH_2.CH(OH).CH_2—O—$$

said gel having a content of hydroxyl groups of at least 15% of the weight of the dry gel and a water regain within the range of from about 1 to 50 g./g. of the dry gel product.

Another example is a gel produced by reacting white commercial dextrin having an average molecular weight in the range of about 20,000 to 50,000 with epichlorohydrin which results in a copolymerizate consisting of a three dimensional macroscopic network, built up of chains of mainly alpha-1,4-glycosidically bonded glucose residues bound together by ether bridges of the type

$$—O—CH_2.CH(OH).CH_2—O—$$

This gel has a hydroxyl group content of at least 15% of the weight of the dry gel and a comparatively low water regain substantially within the range 1–20 g./g. of the dry gel product.

Similarly, a gel product of the same fundamental structure may be obtained from potato starch and epichlorohydrin, but this gel has a higher water regain within the range of 10–50 g./g. of the dry gel product.